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(54) Title: NEW POLYMER MATERIAL FOR ELECTROLYTIC MEMBRANES IN FUEL CELLS

$$MeOH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

$$^3/_2 O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$$

$$MeOH + ^3/_2 O_2 \rightarrow CO_2 + 2H_2O$$
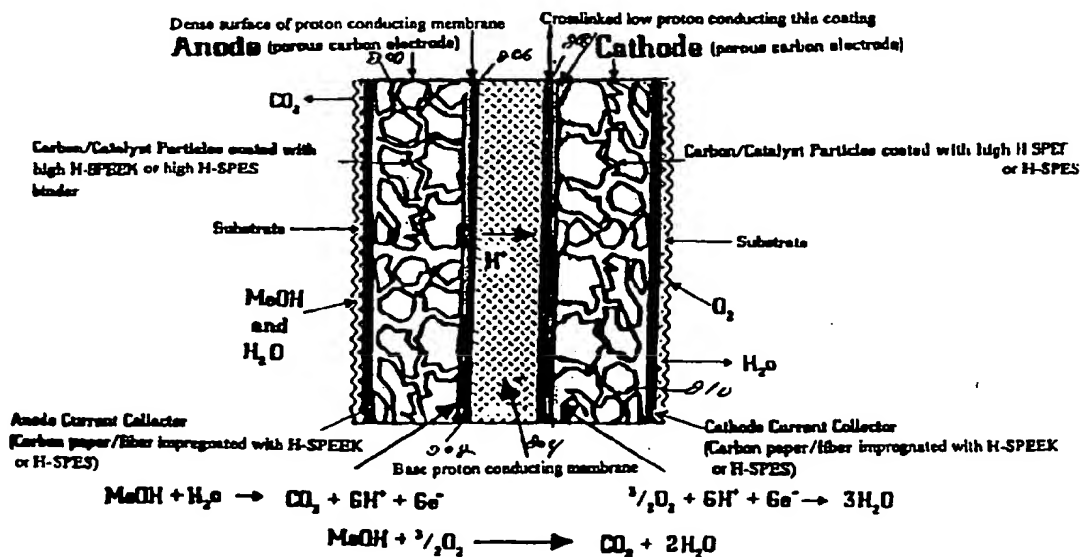
(57) Abstract

A sulfonic acid polymer is processed so that it can be used as a proton conducting membrane for a fuel cell. Asymmetric properties are formed. The preferred fuel cell assembly includes an anode which is a porous carbon-electrode including carbon/catalyst particles coated with the processed sulfonic acid polymer. The anode current collector (202) includes carbon paper fiber impregnated with the processed sulfuric acid polymer. Proton conducting membrane (204) adjoins the cathode (206). The proton conducting membrane includes a dense surface of proton conducting membrane (206) facing the anode (200). The surface (208) facing the cathode (210) is preferably a very thin layer of cross-linked low proton conducting surface.

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NEW POLYMER MATERIAL FOR ELECTROLYTIC
MEMBRANES IN FUEL CELLS

Origin of Invention

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Public Law 96-517 (35 USC 202) in which the Contractor has elected to retain title.

Field of the Invention

The present invention describes a new specialized polymer material, and its use in fuel cells which rely on oxidation- reduction reactions. More specifically, the present invention describes special materials which have proton conducting properties, and are suitable for use as electrolytic membranes in methanol oxidizing reducing fuel cells.

Background and Summary of the Invention

Many electro-chemical oxidation reduction-driven applications require proton conductive materials. One specific fuel cell of this type is described in our U.S. Patent No. _____, based on Serial No. 08/135,007, the disclosure of which is herein incorporated by reference.

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That patent describes a breakthrough in aqueous methanol-based fuel cells.

This special aqueous-methanol fuel cell is the first practical fuel cell to operate without an acid

5   electrolyte. Like many other fuel cells, however, this fuel cell requires a proton conducting membrane. The operation of the fuel cell is shown in Figure 1 and briefly described with reference thereto. Since the present inventors include inventors of the fuel cell

10 described with reference to Figure 1, no admission or implication should be taken from this application that this application represents prior art.

At the time of the writing of this application, a preferred material for a proton conductivity was a per-

15 fluorinated proton-exchange material formed of a co-polymer of tetrafluoroethylene and perfluorovinylether sulfonic acid available from DuPont under the brand name Nafion ™. Nafion 117 ha been used extensively for a proton-conducting membrane.

20   Nafion, however, raises its own host of problems. It is very expensive -- Nafion costs $700 per square meter and at the time of writing of this patent application is more expensive per pound than platinum. Nor is Nafion ideal for its intended purpose. Nafion is

25 quite sensitive to high heat, and can only be used effectively at temperatures below 90 to 100°C. These

lower temperatures prevent fuel cells from being operated at their otherwise optimal temperatures of 270° - 300°C.

Another problem with Nafion is its methanol permeability which allows a substantial amount of fuel

5 crossover across the membrane as described above. Fuel can cross over: it passes across the anode, through the proton conducting membrane (Nafion), to the cathode. The fuel is then oxidized at the cathode instead of at the anode. Nafion's methanol permeability hence allows

10 methanol to cross over and oxidize at the cathode. A mixed reaction (oxidation and reduction) develops on the cathode side, reducing the reaction efficiency. The inventors recognized that this methanol permeability lowers the efficiency of a methanol-based fuel cell.

15 Nafion's is intended to be used at temperature less than around 100°C. A fuel cell operating at a higher temperature, however, in the 200° to 300°C range, would have a higher rate of oxygen reduction and a simultaneously-lowered activation energy of the chemical

20 reaction. This higher temperature also increases the catalytic activity of the platinum catalyst. This is important, since the platinum catalyst proves to be one of the most expensive elements of the preferred fuel cell of the present invention.

25 Nafion also causes problems with water balance. Nafion has a very low rate of water uptake. As a consequence, extreme anode dehydration is caused. Too

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much anode dehydration causes a reduction in the membrane

catalyst continuity. This effectively increases the

resistance between the electrode and the membrane. This

resistance raises the output voltage which needs to drop

5 across the resistance. Heat is produced across the

voltage drop. This also can result in membrane cracking

or pin-holing, and a chemical short-circuit. In the

worst case, the local gas recombination could lead to the

possibility of explosion.

10   It is an object of the present invention to define

new materials for use in such fuel cells. These new

materials have low methanol permeability but high proton

conductivity, and are made from inexpensive, readily

available materials.

15   It is another object of the invention to provide

such materials which are stable at higher temperatures.

According to the present invention, proton conducting

membranes are formed based on a sulfonic acid-containing

polymer. One preferred material is polyether ether

20 ketone or "PEEK". Another is poly (p phenylene ether

sulfone) or "PES". Any sulfonic acid-containing polymer

which has the requisite structural characteristics to act

as a membrane could be used.

          This material is further processed in a way to

25 minimize the methanol permeability. One preferred aspect

modifies the surface to produce asymmetric permeability

properties by controlled cross-linking of sulfonate

- 5 -

groups. The proton conductivity is attained by controlling the degree of sulfonation.

Another aspect modifies the materials using interpenetration polymer materials.

5   Yet another aspect uses zeolites to control the size of interpenetrating materials.

Brief Description of the Drawings

These and other objects of the present invention will now be described in detail with reference to the

10   accompanying drawing, in which:

Figure 1 shows a preferred fuel cell of the present invention;

Figure 2 shows an operational diagram of the fuel cell in use; and

15   Figure 3 shows a basic operation of a fuel cell using the preferred membrane material of the present invention.

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Description of the Preferred Embodiments

Fuel cell

        Fig. 1 illustrates a liquid feed organic fuel cell

10 having a housing 12, an anode 14, a cathode 16 and a

5 solid polymer proton-conducting cation-exchange

electrolyte membrane 18. As will be described in more

detail below, anode 14, cathode 16 and solid polymer

electrolyte membrane 18 are preferably a single multi-

layer composite structure, referred to herein as a

10 membrane-electrode assembly. A pump 20 is provided for

pumping an organic fuel and water solu-tion into an anode

chamber 22 of housing 12. The organic fuel and water

mixture is withdrawn through an outlet port 23 and is re-

circulated through a re-circulation system described

15 below with reference to Fig. 2 which includes a methanol

tank 19. Carbon dioxide formed in the anode com-partment

is vented through a port 24 within tank 19. An oxygen or

air compressor 26 is provided to feed oxygen or air into

a cathode chamber 28 within housing 12. Fig. 2,

20 described below, illustrates a fuel cell system incorpor-

ating a stack of individual fuel cells including the re-

circulation system. The following detailed description

of the fuel cell of Fig. 1 primarily focuses on the

structure and function of anode 14, cathode 16 and

25 membrane 18.

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Prior to use, anode chamber 22 is filled with the organic fuel and water mixture and cathode chamber 28 is filled with air or oxygen. During operation, the organic fuel is circulated past anode 14 while oxygen or air is

5   pumped into chamber 28 and circulated past cathode 16. When an electrical load (not shown) is connected between anode 14 and cathode 16, electro-oxidation of the organic fuel occurs at anode 14 and electro-reduction of oxygen occurs at cathode 16. The occurrence of different

10   reactions at the anode and cathode gives rise to a voltage difference between the two electrodes. Electrons generated by electro-oxidation at anode 14 are conducted through the external load (not shown) and are ultimately captured at cathode 16. Hydrogen ions or protons

15   generated at anode 14 are transported directly across membrane electrolyte 18 to cathode 16. Thus, a flow of current is sustained by a flow of ions through the cell and electrons through the external load.

As noted above, anode 14, cathode 16 and membrane

20   18 form a single composite layered structure. The material of the membrane 18 represents the important subject matter of the present invention.

Anode 14 is formed from platinum-ruthenium alloy particles either as fine metal powders, i.e.

25   "unsupported", or dispersed on high surface area carbon, i.e. "supported". The high surface area carbon may be material such as Vulcan XC-72A, provided by Cabot Inc.,

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USA.   A carbon fiber sheet backing (not shown) is used to
make electrical contact with the particles of the
electrocatalyst.   Commercially available Toray™ paper is
used as the electrode backing sheet.   A supported alloy

5   electrocatalyst on a Toray™ paper backing is available
from E-Tek, Inc., of Framingham, Massachusetts.   Alter-
nately, both unsupported and supported electrocatalysts
may be prepared by chemical methods, combined with
Teflon™ binder and spread on Toray™ paper backing to

10   produce the anode.   An efficient and time-saving method
of fabrication of electro-catalytic electrodes is
described in detail herein below.

Platinum-based alloys in which a second metal is
either tin, iridium, osmium, or rhenium can be used

15   instead of platinum-ruthenium.   In general, the choice of
the alloy depends on the fuel to be used in the fuel
cell.   Platinum-ruthenium is preferable for electro-
oxidation of methanol.   For platinum-ruthenium, the
loading of the alloy particles in the electrocatalyst

20   layer is preferably in the range of 0.5 - 4.0 mg/cm^2.
More efficient electro-oxidation is realized at higher
loading levels, rather than lower loading levels.

Cathode 16 is a gas diffusion electrode in which
platinum particles are bonded to one side of membrane 18.

25   Cathode 16 is preferably formed from unsupported or sup-
ported platinum bonded to a side of membrane 18 opposite
to anode 14.   Unsupported platinum black (fuel cell

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grade) available from Johnson Matthey Inc., USA or

supported platinum materials available from E-Tek Inc.,

USA are suitable for the cathode. As with the anode, the

cathode metal particles are preferably mounted on a

5 carbon backing material. The loading of the

electrocatalyst particles onto the carbon backing is

preferably in the range of 0.5-4.0 mg/cm². The

electrocatalyst alloy and the carbon fiber-backing

contain 10-50 weight percent Teflon™ to provide

10 hydrophobicity needed to create a three-phase boundary

and to achieve efficient removal of water produced by

electro-reduction of oxygen.

During operation, a fuel and water mixture (con-

taining no acidic or alkaline electrolyte) in the concen-

15 tration range of 0.5 - 3.0 mole/liter is circulated past

anode 14 within anode chamber 22. Preferably, flow rates

in the range of 10 - 500 milliliters/min. are used. As

the fuel and water mixture circulates past anode 14, the

following electrochemical reaction, for an exemplary

20 methanol cell, occurs releasing electrons:

$$Anode: \quad CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \tag{1}$$
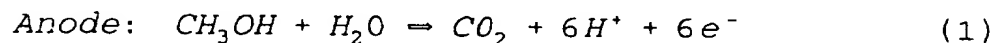
Carbon dioxide produced by the above reaction is

withdrawn along with the fuel and water solution through

outlet 23 and separated from the solution in a gas-liquid

- 10 -

separator (described below with reference to Fig. 2).
The fuel and water solution is then re-circulated into
the cell by pump 20.

Simultaneous with the electrochemical reaction
5 described in equation 1 above, another electrochemical
reaction involving the electro-reduction of oxygen, which
captures electrons, occurs at cathode 16 and is given by:

$$Cathode: \quad O_2 + 4H^+ + 4e^- \Rightarrow H_2O \tag{2}$$
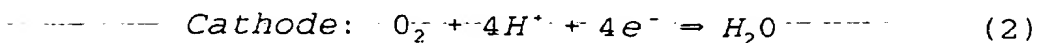
The individual electrode reactions described by
equations 1 and 2 result in an overall reaction for the
10 exemplary methanol fuel cell given by:

$$Cell: \quad CH_3OH + 1.5O_2 \Rightarrow CO_2 + 2H_2O \tag{3}$$
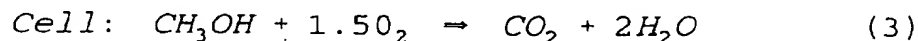
At sufficiently high concentrations of fuel,
current densities greater than 500 mA/cm can be
sustained. However, at these concentrations, a crossover
rate of fuel across membrane 18 to cathode 16 increases
15 to the extent that the efficiency and electrical
performance of the fuel cell are reduced significantly.
Concentrations below 0.5 mole/liter restrict cell
operation to current densities less than 100 mA/cm^2.
Lower flow rates have been found to be applicable at
20 lower current densities. High flow rates are required
while operating at high current densities to increase the

- 11 -

rate of mass transport of organic fuel to the anode as well as to remove the carbon dioxide produced by electrochemical reaction. Low flow rates also reduce the crossover of the fuel from the anode to the cathode

5   through the membrane.

Preferably, oxygen or air is circulated past cathode 16 at pressures in the range of 10 to 30 psig. Pressures greater than ambient improve the mass transport of oxygen to the sites of electrochemical reactions,

10   especially at high current densities. Water produced by electrochemical reaction at the cathode is transported out of cathode chamber 28 by flow of oxygen through port 30.

In addition to undergoing electro-oxidation at the

15   anode, the liquid fuel which is dissolved in water permeates through solid polymer electrolyte membrane 18 and combines with oxygen on the surface of the cathode electrocatalyst. This process is described by equation 3 for the example of methanol. This phenomenon is termed

20   "fuel crossover". Fuel crossover lowers the operating potential of the oxygen electrode and results in consumption of fuel without producing useful electrical energy. In general, fuel crossover is a parasitic reaction which lowers efficiency, reduces performance and

25   generates heat in the fuel cell. It is therefore desirable to minimize the rate of fuel crossover.

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The rate of crossover is proportional to the permeability of the fuel through the solid electrolyte membrane and increases with increasing concentration and temperature. By choosing a sold electrolyte membrane

5 with low water content, the permeability of the membrane to the liquid fuel can be reduced. Reduced permeability for the fuel results in a lower crossover rate. Also, fuels having a large molecular size have a smaller diffusion coefficient than fuels which have small mole-

10 cular size. Hence, permeability can be reduced by choosing a fuel having a large molecular size. While water soluble fuels are desirable, fuels with moderate solubility exhibit lowered permeability. Fuels with high boiling points do not vaporize and their transport

15 through the membrane is in the liquid phase. Since the permeability for vapors is higher than liquids, fuels with high boiling points generally have a low crossover rate. The concentration of the liquid fuel can also be lowered to reduce the crossover rate. With an optimum

20 distribution of hydrophobic and hydrophilic sites, the anode structure is adequately wetted by the liquid fuel to sustain electrochemical reaction and excessive amounts of fuel are prevented from having access to the membrane electrolyte. Thus, an appropriate choice of anode

25 structures can result in the high performance and desired low crossover rates.

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Because of the solid electrolyte membrane is permeable to water at temperatures greater than 60°C, considerable quantities of water are transported across the membrane by permeation and evaporation. The water
5   transported through the membrane is condensed in a water recovery system and fed into a water tank (both described below with reference to Fig. 2) so that the water can be re-introduced into anode chamber 22.

Protons generated at anode 14 and water produced
10 at cathode 16 are transported between the two electrodes by proton-conducting solid electrolyte membrane 18. The maintenance of high proton conductivity of membrane 18 is important to the effective operation of an organic/air fuel cell. The water content of the membrane is
15 maintained by providing contact directly with the liquid fuel and water mixture. The thickness of the proton-conducting solid polymer electrolyte membranes should be in the range from 0.05 - 0.5 mm to be dimensionally stable. Membranes thinner than 0.05 mm may result in
20 membrane electrode assemblies which are poor in mechanical strength, while membranes thicker than 0.5 mm may suffer extreme and damaging dimensional changes induced by swelling of the polymer by the liquid fuel and water solutions and also exhibit excessive resistance.
25 The ionic conductivity of the membranes should be greater than 1 ohm^{-1} cm^{-1} for the fuel cell to have a tolerable

- 14 -

internal resistance. As noted above, the membrane should

have a low permeability to the liquid fuel.

Membrane Formation and Materials

    The present inventors investigated alternative

5 materials in an attempt to obviate these problems. We

found some advantageous materials. These materials and

their formation and processing are described in the

embodiments disclosed herein.

    These materials have two important

10 characteristics: inexpensive starting materials, and

enhanced protection against fuel crossover. Preferably,

methanol transport across the membrane is limited. The

methanol transport limiting can be carried out using one

of the following embodiments.

15   First Embodiment

    An inexpensive sulfonated material, e.g., sulfonic

acid polymer, which is stable and electro-oxidative

condition and susceptible of forming a membrane layer, is

used as a starting material. That material should be

20 inexpensive and also stable at high temperatures. The

inventors recognized the material needs to include an

excess number of proton conductors beyond that which is

rally needed for the proton conduction that is needed by

the fuel cell. Preferably, those excess proton

25 conductors are excess sulfonate groups. According to the

present invention, that material is further processed to

- 15 -

sacrifice some of the proton conductivity capability in a way as a trade off to reduce methanol permeability.

The first preferred material is poly ether ether ketone, "PEEK". PEEK is a temperature resistant and

5   oxidatively stable engineering polymer. PEEK is converted into an asymmetric proton conducting membrane. The asymmetric membrane has spaces which allow protons to pass, but which minimize the amount of methanol molecules which pass. This hence reduces fuel crossover when this

10 membrane is used in a fuel cell.

The methanol permeation is reduced according to this embodiment by surface modifications of the polymer.

The specific operation and results progress as follows. 120 grams of 250p grade PEEK is stirred in 1200

15 ml of concentrated sulfuric acid ~97% (H_2SO_4) at room temperature for 4 1/2 hours. The homogeneous solution resulting from this stirring is then heated to 91°C for 1 hour. The reaction is then quenched and cooled to room temperature.

20 The polymer is then precipitated in ice slurry bath and filtered then washed to remove the excess acid, and to form an appropriate material. At pH 5 the polymer is dried under ambient conditions for 36 to 72 hours. The chemical reaction is given below.

- 16 -
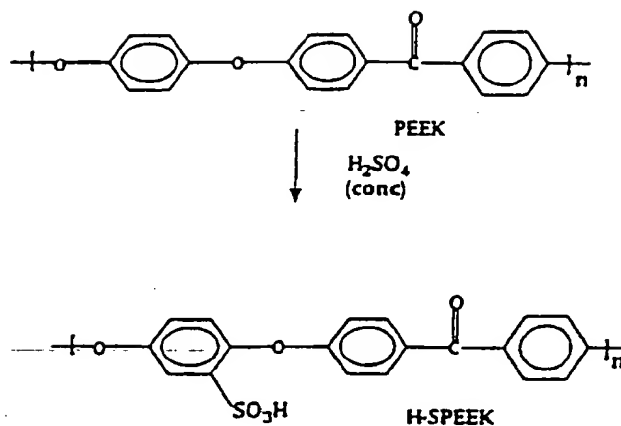
This first step forms high molecular weight

material which we call H-SPEEK. H-SPEEK has an

equivalent weight of 365. Unlike PEEK, H-SPEEK is

5   soluble in an organic solvent and water mixture. One out

of every three benzene rings in the material is

sulfonated with a sulfonate (SO$_3$H) group.

The material is then dried, and then dissolved in

a solvent mixture: preferably an acetone/water mixture.

10 This mixture is further diluted with approximately 10% of

the polymer sample weight of glycerin - here 3 g. The

dissolved-polymer and glycerin mixture is then filtered

over a chelate pack. This filtered mixture forms the

cast film when the solvent is evaporated.

15   The preferred embodiment casts these films in

glass pyrex dishes. Evaporation is carried out over a

evaporation time which ranges between 24 and 48 hours.

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A first technique of this first embodiment cross-
links as follows. After the film has been set, the
entire dish is heated to 120°C under vacuum. The H-SPEEK
formed by the above-discussed process has a large number

5   of sulfonate groups on the benzene rings in the PEEK
polymer chain. On the average, one out of every three
rings include a sulfonate group. The H-SPEEK as formed
in that way has about 365 mass per proton, a much better
figure than Nafion™ which has a much larger value of 1144

10 mass per proton. This represents an excess proton
capacity beyond what is really necessary for operating
the fuel cell.

The inventors recognized that this left enough
sulfonate groups so that some could be sacrificed for

15 cross-linking. Even after further processing, the
polymer maintains less than 600 mass per proton. The
inventors recognized that even though there is a lot of
cross-linking in the present invention, there is still a
large amount of proton conductivity.

20   As described herein, even after further
processing, the polymer maintains less than 600 mass per
proton. The inventors recognized that even though there
is a lot of cross-linking in the present invention, there
is still a large amount of proton conductivity.

25   The heating at 120°C under vacuum causes cross-
linking shown below.

- 18 -

O = S = O   O = S = O
     \   /
     O-H   H-O

O
‖
S
‖
O
+
H_2SO_4
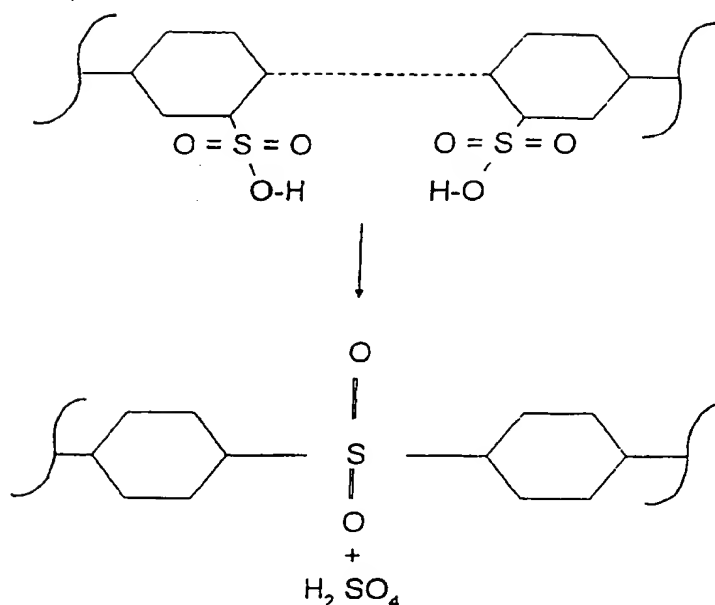
A nuclear magnetic resonance ("NMR") analysis of the sulfonic acid groups in the uncross-linked film was made. The NMR solution spectrum monitored ^1H in

5 deuterated dimethylsulfoxide ($_{d6}$DMSO) indicated one sulfonic acid group per repeat unit, where each repeat unit is as shown above in reaction 1, including three benzene rings.

A series of solutions that can contain the cross-

10 linked membrane was back-titrated with a standard dilute solution of sodium hydroxide. The analysis of the titration indicated that after cross-linking, 28% of the sulfonic acid groups in the total solution had been converted to sulfone groups by the cross-linking process.

15   When sulfonating the PEEK, the inventor found that a trade-off was necessary between the amount of sulfonation and the necessity for a stable physical

- 19 -

structure. More sulfonic acid improves the proton conducting performance. However, it also correspondingly degrades the physical structure of the resulting membrane. The inventors therefore developed a trade-off

5 between the amount of sulfonation and the appropriate physical structure. They found that sulfonating one out of every three benzene rings provides the best trade-off between the two competing objectives.

The materials formed herein are preferably
10 surface-dense. It was found that the surface-dense samples prepared by this process were comparable to commercial Nafion in mechanical strength and proton conductivity. These materials had a large number of. sulfonic acid groups than Nafion. The cross-linking

15 could therefore be carried out without significant loss of proton conductivity.

These surface-dense materials form an asymmetric membrane. Importantly for present purposes of the present invention, the material will allow water to pass,
20 and has proton conductivity. However, the spaces between parts of the material are small enough to hinder the methanol (CH_3OH) from passing.

A second material embodiment of the present invention uses a different sulfonic acid polymer.

25   Poly (p-phenylene ether sulfone) or PES which is a liquid crystal polymer has the structure

- 20 -
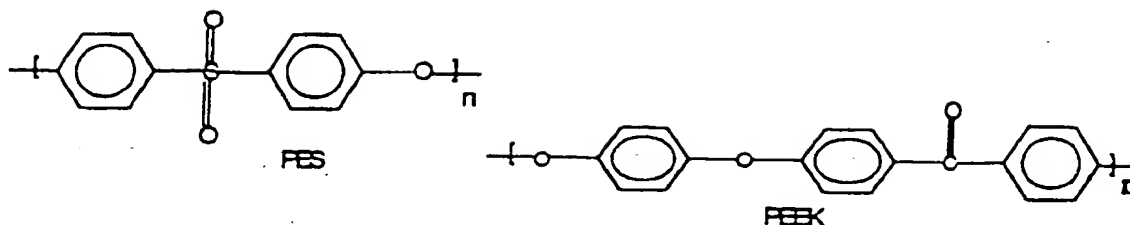
The operation on the PES is quite analogous to that of
the PEEK described above. PES's glass transition
temperature is 225°C, as compared with PEEKs glass
5 transition temperature of 156°C. The price of PES is
about $10 lb: an order of magnitude less than Nafion.
The sulfonation occurs as follows
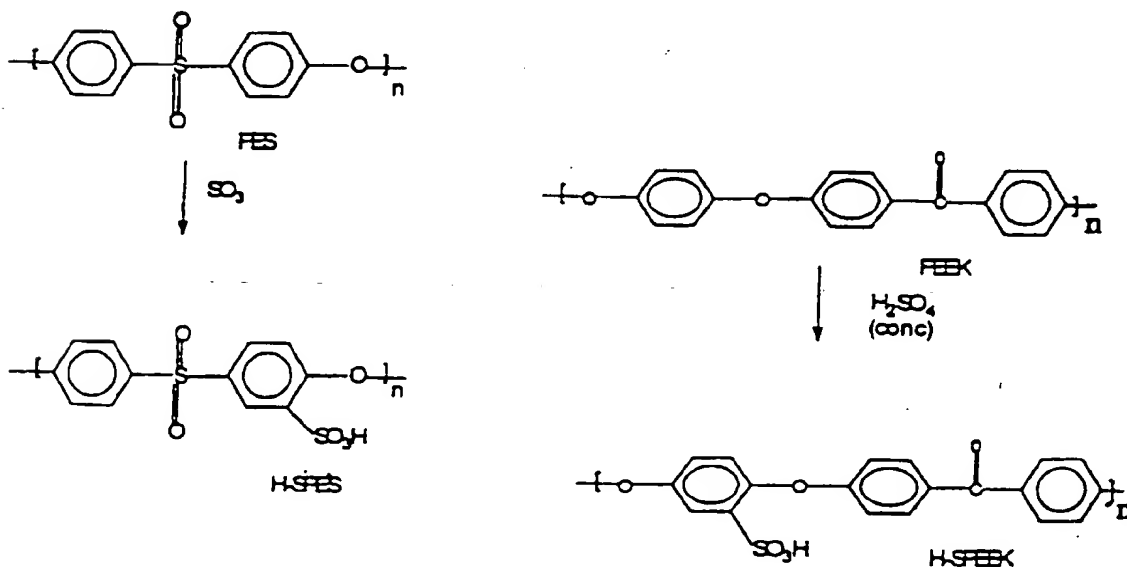
H-SPES-like H-SPEEK, requires a trade-off between
10 the amount of sulfonation and its physical structure.

- 21 -

Below 30% sulfonation, both materials act as ionimers.
Above 70% sulfonation, these materials act as
polyelectrolytes or PEs. By controlling the degree of
sulfonation, the H-SPES film properties can be optimized:
5 ease of film fabrication, strength and conductivity of
the H-SPES film can be controlled and optimized.

An important property of both these materials as
processed above is their large number of sulfonic acid
groups allow sacrifice of sulfonic acid groups for appro-
10 priate cross-linking. It has already been described
above that the H-SPEEK materials had 365 mass per proton.
When cross-linked, these materials still have 504 mass
per proton. This compares quite favorably with Nafion
film's 1144 mass per proton. In addition, the sulfonic
15 acid groups in H-SPEEK are located in the H-SPEEK
backbone. This type of polyelectrolyte film is well-
known to contain functional channel structures for proton
conduction.

Two other alternative techniques are possible
20 according to this first embodiment. A first technique
varies the amount of water and organic solvents used as
polymer solvents during the film casting process. As
described above, the characteristics of these materials
change based on the amount of sulfonation and nature of
25 the solvent during the membrane fabrication. According
to this aspect of the present invention, the amount of
water is lowered or eliminated from H-SPEEK film casting

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solution during the time when the surface of the film is being cast. This cases a dense-surface area on the resulting film.

Another alternative technique forms two separate
5   films: a first film which acts as the base backbone, and a second film forms low proton concentration coating on the base conducting membrane. This low proton concentration H-SPEEK or H-SPES is then cross-linked by heating under vacuum to form an anisotropic composite
10 membrane. This forms an asymmetric membrane.

To summarize: ⟵ ρ ω.ιs

The first embodiment uses a process of surface modifying the material. The present embodiment preferably modifies only one "side" of the materials and
15 not the other side. This asymmetric modification provides a surface-dense anisotropic membrane. That surface-dense membrane faces the anode to minimize methanol cross-over.

The modification of surface morphology can be
20 carried out by varying the proportion of water and organic solvent used as polymer solvent. This allows modifying the rate of solvent evaporation during the film casting process.

An alternate technique is to heat the surface to
25 cause polymer cross-linking.

An alternate technique of modification of surface morphology applies a thin, low proton concentration H-

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SPEEK or H-SPES coating on the base conducting membrane
as shown in Figure 3.   Cross-linking of this thin coating
can have similar effects to those discussed above.

Second embodiment

5   The methanol transport is limited according to
this second embodiment by optimizing hydrophobic and
hydrophilic polymer chain interactions.   Proton-
conducting inter penetration polymer networks are formed
by using a combination of these structures.

10   The second embodiment forms a similar starting
compound to that described above.

.The second type of structural modification
according to the present invention which forms an
asymmetric membrane by modifying the highly sulfonated
15 PEEK or PES to form an inter-penetrating polymer network.
This proton conducting membrane system forms from two
types of proton conducting polymer network.   The type I
membrane forms from a cross-linked hydrophobic polymer
chain and inter-penetrating with another cross linked
20 hydrophilic polymer chain as described above.   This type
I membrane has a variable amount of low sulfonated H-
SPES.   It also has cross-linked hydrophobic polymer
chains of highly sulfonated H-SPEEK.

The type II membrane has cross-linked hydrophobic
25 varying low sulfonated H-SPEEK as well as cross-linked
hydrophilic highly sulfonated H-SPES.   Both materials

- 24 -

have their chemical structure modified according to the
following:
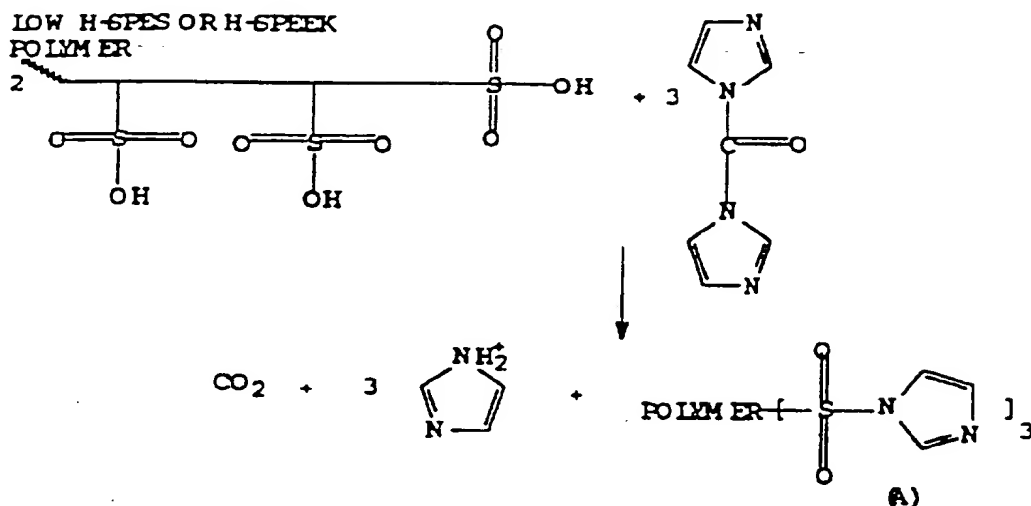
The highly sulfonated H-SPEEK or H-SPES can be cross-
5 linked at high temperature according to the reaction
mechanism previously shown.

Type I film is formed from a film casting solution
mixture including compound A, compound B, and highly sul-
fonated H-SPEEK or H-SPES. Type II material with inter-
10 penetration polymer networks is formed of hydrophobic H-
SPEEK and hydrophilic H-SPES. This can also be prepared
using the same method. This effectively causes two
different kinds of polymers, with different chemical
properties. Both have proton conductivity, but both have
15 different structures. These different structures have
been found to minimize the fuel crossover.

Third embodiment

- 25 -

The third embodiment modifies free volumes in proton conducting membranes. These free volumes can be reduced by preparing small particle-size-selected zeolites-preferably mordenite. This does not occlude methanol, but does have proton conductivity.

A zeolite material is added to the H-SPEEK or H-SPES to form a zeolite/H-SPEEK or zeolite/H-SPES composite membrane. The proton-containing H-SPEEK and H-SPES, as well as the proton in the hole of zeolite will cause proton conductivity.

The preferred zeolite used according to this embodiment is proton containing mordenite. The mordenite is added to the HSPEEK or HSPES proton conducting composite membrane. The inventor found that this reduces the free volume of the membrane, and therefore also reduces the methanol crossover.

Mordenite has the function of selectively adsorbing or rejecting different molecules. The ionic conductivity of mordenite is depending on the nature of the cation and the water concentration.

For example, mordenite which has a lot of tin therein. So called "tin-rich mordenite" is highly conducting. Calcium and BA rich mordenites do not include methanol, because the diameters of the narrowest cross-section of the interstitial channel is between 3.48 and 4.0 angstroms. Mordenite is very stable in acid solutions of around pH 0.75.

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Mordenite is well described in the literature.
Any described zeolite material can be used. The
inventors believe that the best mordenite will include H⁺.

The preferred fuel cell final assembly is shown in
5   Fig. 3. This includes an anode which is a porous carbon
electrode including carbon/catalyst particles coated with
the materials of the present invention. The anode
current collector 202 includes carbon paper fiber
impregnated with the material. Proton conducting
10 membrane 204 of the present invention adjoins the cathode
206. The proton conducting membrane preferably includes
a dense surface of proton conducting membrane 206 facing
the anode 200. The surface 208 facing cathode 210 is
preferably a very thin layer of cross-linked low proton
15 conducting surface.

The cathode 210 includes carbon catalyst particles
also coated with high H-SPEEK or H-SPES.

Although only a few embodiments have been
described in detail above, those having ordinary sill in
20 the art certainly understand that many modifications are
possible in this preferred embodiment without departing
from the advantageous structure of the present invention.
For example, while H-SPEEK and H-SPES have been described
above as being the preferred materials, it should be
25 understood that other alternative materials can also be
used. Any similar material which is capable of
sulfonation and cross-linking can be used in place of the

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H-SPEEK or H-SPES. The specific kind of inter-
penetrating polymer which is used is only exemplary, and
it should be understood that other inter-penetrating
polymers could be used. Moreover, the zeolite could be
5 any zeolite which forms the necessary function, and the
criteria for choosing an appropriate zeolite have been
described above.

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What is claimed:

    1.   A method of forming a proton conducting polymer film, comprising:

        preparing a sulfonic acid polymer material
5 which can be treated to form a material with proton conducting characteristics,

        treating said material to enhance its proton conducting characteristics in a way to produce excess proton conductivity; and

10   further treating said material in a way to link together some but not all of the elements which carry protons, to form a denser but still stable membrane.

    2.   A method as in claim 1, wherein said treating
15 comprises treating the material to add sulfonate groups thereto.

    3.   A method as in claim 2, wherein said further treating comprises cross-linking the sulfonate groups.

    4.   A method as in claim 2, wherein said further
20 treating comprises cross-linking the sulfonate groups on one surface only, and not on the other surface to form a material which has asymmetric surface-dense characteristics.

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5.   A method as in claim 4, wherein said material
is poly ether ether ketone.

6.   A method as in claim 4, wherein said material
is p-phenylene ether sulfone.

5   7.   A method as in claim 3, wherein said cross-
linking follows the chemical reaction that
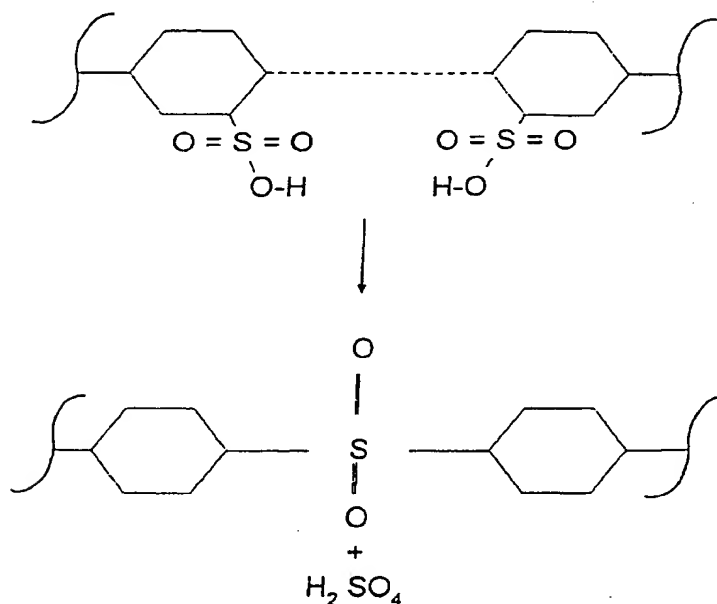
8.   A method as in claim 1, wherein said further
treating forms a denser and stable membrane which has
10   materials therein which allow water and protons to pass,
but which occludes methanol compounds from passing.

9.   A method of forming a proton conducting
polymer film for use in a methanol based fuel cell,
comprising:

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preparing a sulfonic acid polymer material which can be treated to form a material with proton conducting characteristics;

treating said material to enhance its proton 5 conducting characteristics in a way to produce excess proton conductivity; and

adding an additional material to the material which further enhances methanol occlusion.

10. A method as in claim 9, wherein said further 10 material is a material including inter-penetration polymer network.

11. A method as in claim 9, wherein said material includes zeolites.

12. A method as in claim 11, wherein said 15 zeolites include mordenite having a characteristic to occlude methanol but not occlude water or protons.

13. A proton-conducting polymer film, comprising:

a sulfonic acid polymer material, having sulfonate groups therein, and formed with a first surface 20 and an oppositely facing second surface, said first surface having cross-linked sulfonates therein, and an amount of cross-linking in said first surface being more than an amount of cross-linking in said second surface.

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14. A film as in claim 13, wherein said polymer
materials includes benzene rings therein, and
approximately one benzene ring per each repeating unit of
the polymer chain includes a sulfonate group thereon.

5   15. A film as in claim 14, wherein said polymer
material is PEEK.

16. A film as in claim 14, wherein said polymer
material is PES.

17. A fuel cell electrode/membrane assembly,
10 comprising:

an anode material, formed of a material to
carry out an oxidation reaction;

a proton conducting polymer membrane
material, connected to said anode material, said proton
15 conducting polymer membrane material including sulfonate
acid polymer with sulfonate groups thereon, and having a
first surface attached to said anode assembly, and a
second surface facing away from said anode assembly, said
first surface including elements therein which
20 asymmetrically effect a propensity of said first surface
to conduct materials as compared with said second
surface; and

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a cathode, connected to said second surface, said cathode of a type for allowing a reduction reaction to be carried out thereat.

18. An assembly as in claim 17, wherein said
5 anode and cathode are optimized to carry out oxidation of aqueous methanol.

19. An assembly as in claim 17, wherein said polymer membrane is a selectively sulfonated membrane, having one sulfonate group attached to approximately one
10 benzene ring per each repeating unit of the polymer chain, and including cross-linked structure therein including cross-linked sulfonate groups of the chemical form

$$\text{benzene ring} - \overset{\displaystyle O}{\underset{\displaystyle \underset{+}{O}}{\overset{\displaystyle \|}{\underset{\displaystyle \|}{S}}}} - \text{benzene ring}$$

$$H_2 SO_4$$
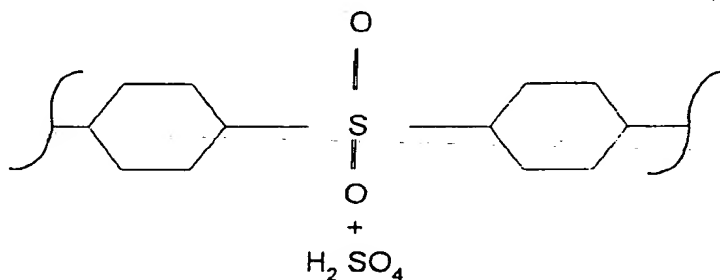
15   20. An assembly as in claim 19, wherein said polymer membrane is SPEEK.

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21.   An assembly as in claim 19, wherein said polymer material is SPES.

22.   An assembly as in claim 17, wherein said first surface includes a dense surface of cross-linked
5 structures.

23.   A method of forming an asymmetric proton-conducting polymer film, comprising:

obtaining a polymer material of a type which can be sulfonated;

10   selectively sulfonating said polymer film, to an amount which would conduct more protons than those needed for an application;

cross-linking some of said sulfonate groups in a way such that the cross-linked sulfonate groups will
15 not conduct protons; and

using un-cross-linked sulfonate groups to conduct protons.

24.   A method as in claim 23, wherein said cross-linking is carried out by heating said surface.

20   25.   A method as in claim 23, wherein said material is obtained by

dissolving H-SPEEK into a solvent,

removing solvent,

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casting a film from the H-SPEEK solution after removing the solvent; and

heating the resulting dry film in vacuum above 100°C to produce a cross-linked proton conducting
5 membrane.

26. A method as in claim 23, wherein said material is obtained by

dissolving H-SPES into a solvent;

removing solvent;

10 casting a film from H-SPES solution after removing the solvent; and

heating the resulting dry film in vacuum above 100°C to produce cross-linked proton conducting membrane.

27. A proton conducting polymer film for a
15 methanol oxidation/reduction fuel cell, comprising:

a sulfonic acid polymer, processed to have an effective number of sulfonic acid groups per nonsulfonic acid groups to balance between proton conductivity and physical structure stability, said sulfonic polymer
20 further processed to selectively allow water and protons to pass therethrough, but to occlude methanol compounds from passing therethrough.

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28. A polymer as in claim 27, wherein said structure of the further processing includes cross-linked sulfonate groups of the form

$$\text{──}\bigcirc\text{──}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}\text{──}\bigcirc\text{──}$$
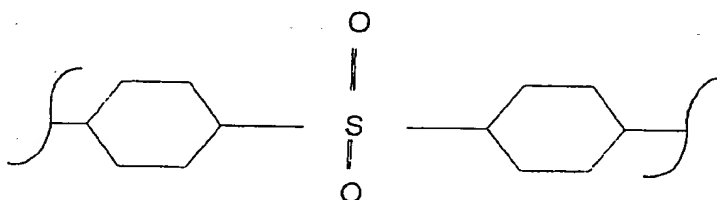
5   29. A polymer as in claim 27, wherein the structure is formed by said further processing a combination formed between hydrophobic and hydrophilic polymer chain interactions.

        30. A polymer as in claim 29, wherein said
10 polymer chain interactions is formed by proton conducting inter-penetration polymer networks.

        31. A polymer as in claim 27, wherein said occluding is carried out by limiting a size of free volumes in the proton conducting membrane.

15   32. A polymer as in claim 31, wherein said size is limited by cross-linked compounds.

        33. A polymer as in claim 31, wherein said size is limited by adding particle size-selected zeolites.

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34.   A method of limiting fuel crossover in a
methanol fuel cell, comprising:

        providing an anode in contact with a fuel
including a methanol derivative compound;

5   providing a cathode in contact with reduction
materials;

        using a proton conducting polymer film
between said anode and cathode, to conduct protons and
water from said anode to said cathode; and

10   limiting a free volume in said polymer film
to prevent fuel from crossing between said anode and
cathode.

        35.   A method as in claim 34, wherein said polymer
film is a sulfonic acid polymer.

15   36.   A method as in claim 35, wherein said
sulfonic acid polymer includes benzene rings therein, and
wherein said sulfonic acid polymer includes approximately
1 sulfonic acid group per benzene ring per each repeating
unit of the polymer chain.

20   37.   A method as in claim 35, further comprising
cross-linking sulfonic acid groups of the sulfonic acid
polymer according to the formula

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$$O$$
$$\|$$
$$S$$
$$\|$$
$$O$$

$$+$$

$$H_2 SO_4$$
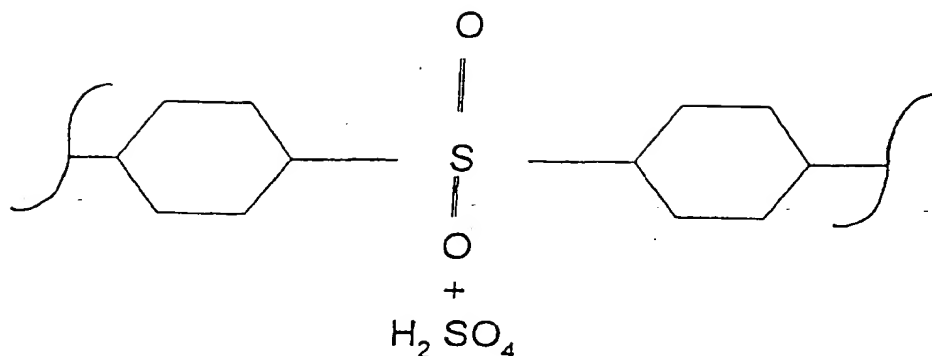
38. A method as in claim 35, further comprising adding particle size selected materials to said sulfonic acid polymer to occlude methanol compounds.

39. A method as in claim 38, wherein said
5 particle size selected compounds include particle size selected zeolites.

40. A method as in claim 39, wherein said particle size selected zeolites include mordenite and mordant.

10   41. A method as in claim 35, wherein said sulfonic acid polymer has less than 600 mass per proton.

42. A method of forming an asymmetrical conducting sulfonic acid polymer film, comprising:
       obtaining a first sulfonic acid polymer;

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processing said sulfonic acid polymer to add
sulfonic acid groups thereto in an effective amount to
allow proton conduction; and

modifying a morphology of the resultant
5 compound to limit the transport of methanol across the
membrane more than a limiting proton or water conduction
across the membrane.

43. A method as in claim 42, wherein said
morphology modification comprises cross-linking materials
10 on a first surface of the membrane.

44. A method as in claim 42, wherein said
morphology modification comprises varying a proportion of
water to solvent.

45. A method as in claim 42, wherein said
15 morphology changing comprising adding a proton conducting
inter-penetration polymer network.

46. A method as in claim 42, wherein said
morphology modification comprises adding particle size
selected materials.

20   47. A method as in claim 46, wherein said
particle size selected materials are zeolites.

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48.   A method as in claim 46, wherein said
zeolites include mordenite or mordant.

49.   A method of forming a proton conducting
polymer film, comprising:

5   preparing a sulfonic acid polymer material
from the group consisting of poly ether ether ketone or
p-phenylene ether sulfone;

                treating said sulfonic acid polymer to form a
material with proton conducting characteristics;

10   forming said material into a membrane; and

                further treating said material in a way to
change its characteristic in a way to allow proton
conduction but to minimize conduction of larger
materials.

FIG. 1

FIG.2

Dense surface of proton conducting membrane

Crosslinked low proton conducting thin coating

Anode (porous carbon electrode)

Cathode (porous carbon electrode)

Carbon/Catalyst Particles coated with high H-SPEEK or H-SPES

Carbon/Catalyst Particles coated with high H-SPEEK or high H-SPES binder

Substrate

Substrate

CO_2

O_2

H_2O

MeOH and H_2O

Anode Current Collector
(Carbon paper/fiber impregnated with H-SPEEK or H-SPES)

Cathode Current Collector
(Carbon paper/fiber impregnated with H-SPEEK or H-SPES)

H^+

Base proton conducting membrane

$MeOH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

$^3/_2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

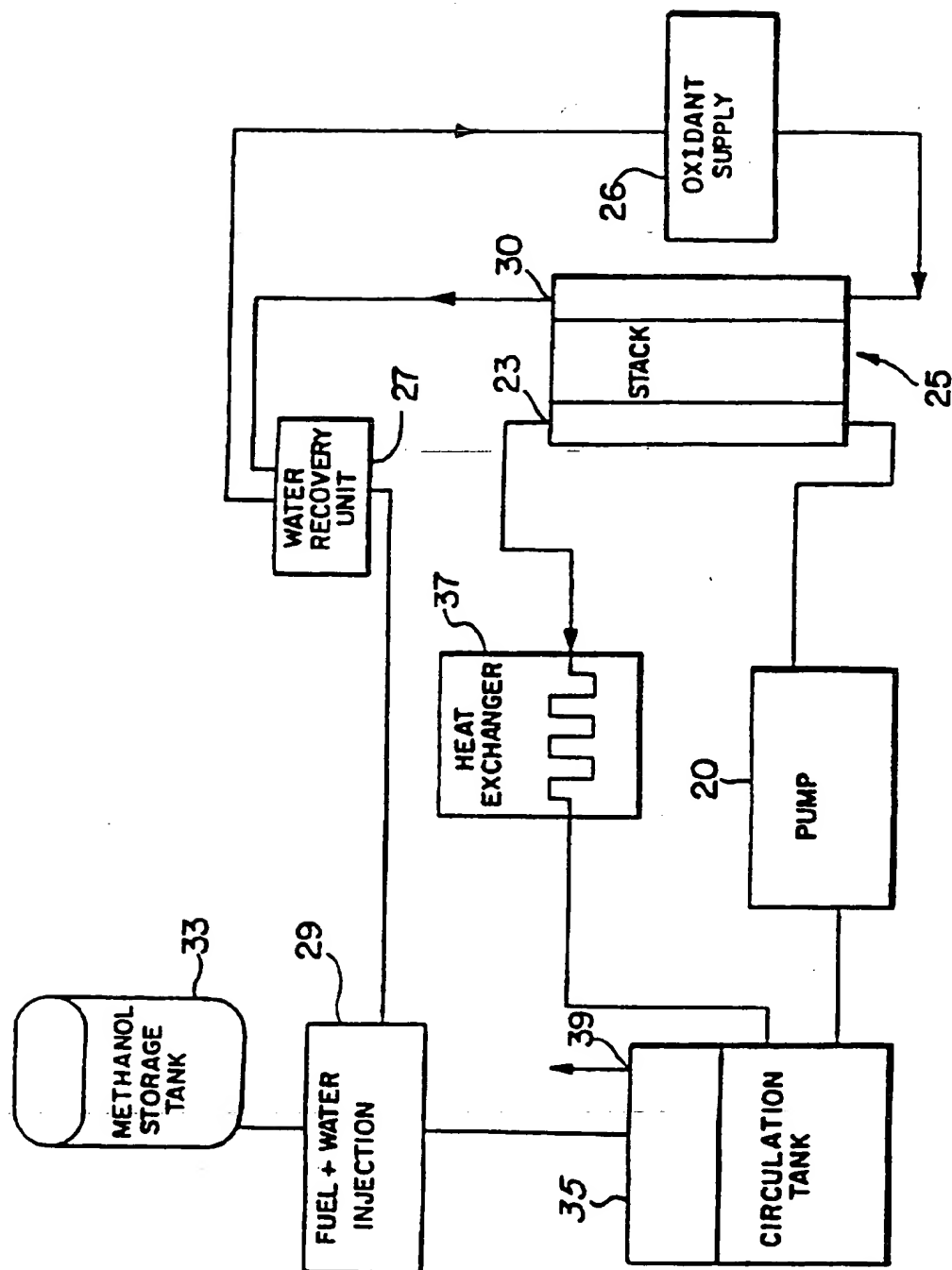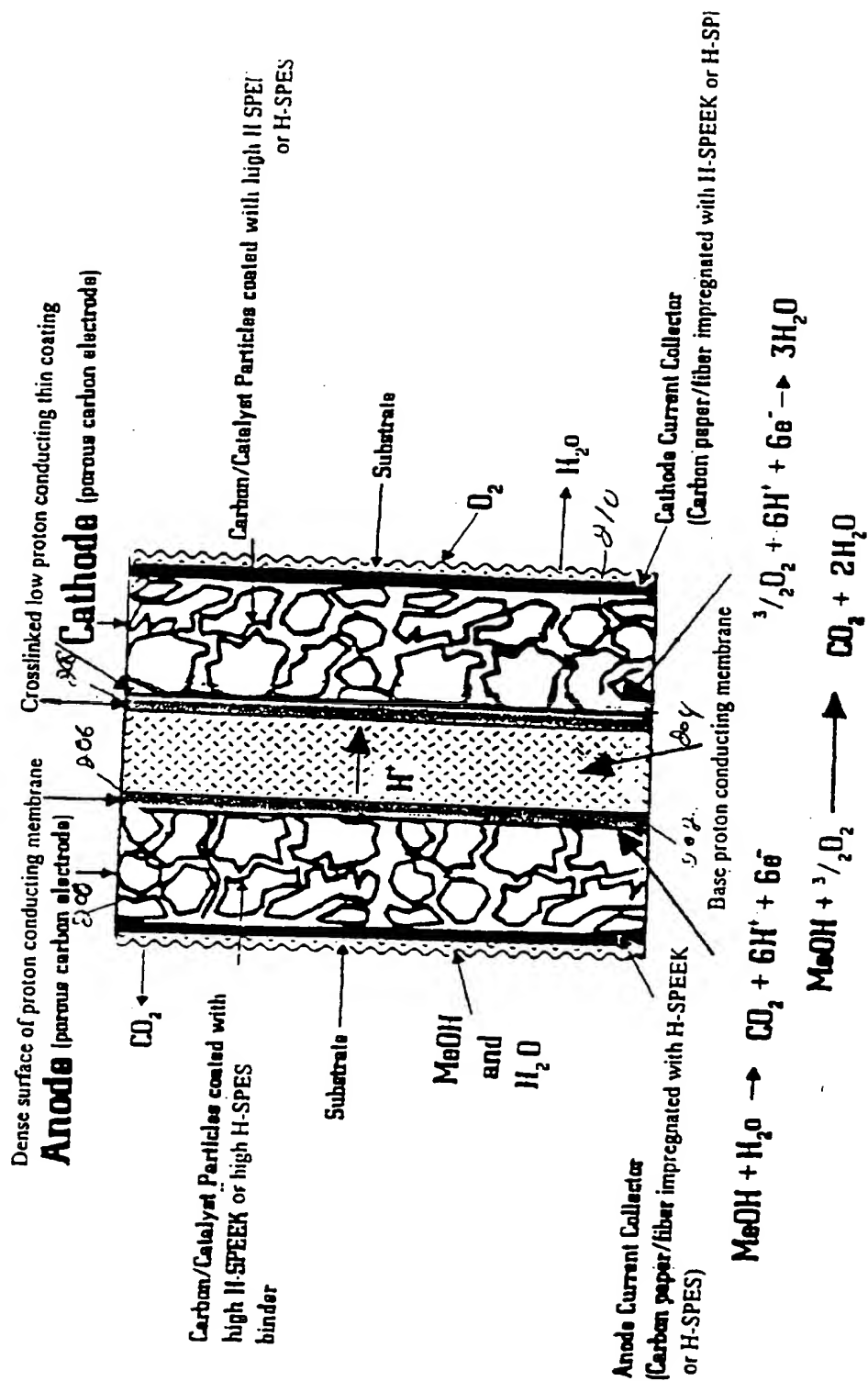$MeOH + ^3/_2O_2 \rightarrow CO_2 + 2H_2O$

FIGURE 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/18823

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6)   :H01M 8/10, 8/22; C08J 5/18
US CL   :429/42, 17, 33, 192; 252/62.2; 521/27, 30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/42, 17, 33, 192; 252/62.2, 500, 518, 521; 521/27, 30

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,468,574 A (EHRENBERG et al) 21 November 1995, see abstract and col. 12, lines 48-58.	1-3, 7-9, 17, 19, 22-24, 27-29, 31, 32, 34-37, 41-44, 49
A		4-6, 10-16, 18, 20, 21, 25, 26, 30, 33, 38-40, 45-48
A	US 4,711,907 A (STERZEL et al) 08 December 1987, see abstract.	1-49

[X] Further documents are listed in the continuation of Box C.   [ ] See patent family annex.

<table>
<tr><td>*</td><td>Special categories of cited documents:</td><td>"T"</td><td>later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td></tr>
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</table>

Date of the actual completion of the international search	Date of mailing of the international search report
31 MARCH 1997	2 4 APR 1997

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Form PCT/ISA/210 (second sheet)(July 1992)*